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Abstract

The complexation of redox sensitive elements by humic acid (HA), described through the charge neutralisation model (CNM) has been reviewed in order to have a comprehensive scope. The data acquired in HUMICS program on thorium (IV), and data available in the literature, were reinterpreted according to the CNM, and adapted to uranium (IV), neptunium (IV) and plutonium (IV) through analogy in order to draw a boundary prediction. Otherwise, available data obtained in the framework of the CNM were used, or adapted if necessary, for other redox states when the analogy is justified, *i.e.* Am^{3+}-Cm^{3+} for Pu^{3+}, NpO_2^+ for PuO_2^+ and UO_2^{2+} for PuO_2^{2+}.

The obtained speciation diagrams indicate that, when (HA) = 100 mg/L, redox sensitive actinides should be reduced to their +IV state when $E_H \leq 650$ mV/SHE for plutonium, $E_H \leq 100$ mV/SHE for neptunium and $E_H \leq -20$ mV/SHE for U. Plutonium could be present as mixtures of plutonium (III) and (IV) depending on the pH value in reducing ground waters $-150 \leq E_H$ (mV/SHE) ≤ 150. The known reduction of neptunium (V) to neptunium (IV) in Gorleben ground waters seems also well represented, so does the stability of uranium (VI) in humic solution when $E_H \geq 100$ mV/SHE. Conversely, the known association of plutonium (VI) in marine systems are not satisfactorily represented, so does is the uranium behaviour under reducing conditions. Experiments under well-controlled conditions are still needed to ascertain the plutonium and uranium comportment in the presence of humic acid.

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1. Introduction

The aqueous chemistry of actinide elements is one of the most intricate and interesting chapters of the general chemistry of these elements. In particular, uranium, neptunium and plutonium are redox sensitive in aqueous solutions, and the study of their complexation properties has been a challenging puzzle for generations of scientists. As the reduced states are difficult to stabilise in solution, there is a large discrepancy between the different published values of complexation constants. Therefore, the use of analogies is a convenient way to estimate unknown complexation constants [1], knowing the limitation of the approach [2].

The complexation of actinides by humic substances (HS), which represent about 40-60 % of the natural organic matter (NOM), is not an exception. Humic substances are the alkaline extracted fraction of the NOM. From this primary fraction are extracted three sub-fraction namely: humine that is insoluble at whatever pH; humic acids (HA) that are not retained on a hydrophobic resin and insoluble at acidic pH; fulvic acids (FA) that are retained on a hydrophobic resin and are soluble at whatever pH.

A lot of works have been undertaken on "stable" redox states, *i.e.* uranium (VI), neptunium (V) and americium/curium/europium (III). Experimental difficulties have often prevented from obtaining reliable results on reduced states of uranium, neptunium or plutonium. Furthermore, the redox properties of humic substances [3-5] have led to confusing results for protactinium [6], neptunium [7, 8], plutonium [9-12] and other elements [13-19], even if the use of ligands to stabilise redox state is well known in the nuclear industry [20-23]. Otherwise, the reduction of uranium (VI) by HS has not been clearly observed up to now [24-26].

The complexation of metals by humic substances has been a subject of extensive works in the past decades. The main problem concerning thermodynamic descriptions of humic complexation is the apparent increasing complexation strength with pH. This phenomenon is related to the increasing ionisation of functional groups ("carboxylic" and "phenolic") with increasing pH. This increasing complexation strength was modelled using either global varying complexation coefficients [25, 27],[1] varying number of sites [28], multi-pKa approaches [29], and statistical description [30-32]. The latter type of model could be seen as more representative of the aggregate structure of HS [33, 34], and could account for competition with other metals more accurately [31, 32, 35]. Nevertheless, the more operational type of description has been widely applied to actinides and a large number of data are available in literature.

The charge neutralisation model (CNM) [28] has been applied to a lot of relevant actinides namely uranium (VI) [24, 36], neptunium (V) [37-39], americium, curium and

[1] This implies that the "constants" are not "real" thermodynamic constants.

europium (III) [40-43]. The variation of the number of available sites can be seen as a continuous term. Only few attempts have been reported up to now in the intricate cases of actinides (IV) and plutonium [44]. Even if the strong interaction of actinide (IV) with HS is known [36, 45-49], the available data on humic complexation are scarce. Nash and Choppin, more than twenty years ago in the framework of a polyelectrolytic model,[2] obtained high interaction parameters for thorium (IV) between pH 3.9 and 5 for different humic and fulvic acids [50]. Recently, data has been obtained under neutral pH conditions [44, 51].

The interactions with neptunium and plutonium are more confusing as HS induce redox reactions [6, 9-11]. Nevertheless, the complexing properties of HS towards almost all of the redox analogues of these elements have received great attention.

The aim of this exercise is to reinterpret and adapt the available data in the literature in the framework of the CNM in order to define the scope of humic complexation of redox sensitive elements.

2. Treatment of data

Only the complexing properties of HS will be considered here, since their reducing properties have not totally been clarified.

2.1. CNM model

The description of the CNM has been done elsewhere and will not be completely developed here [28]. Through this model, the increasing complexation strength with pH is managed through a varying parameter LC, the loading capacity, which represents the maximum fraction of the humic sites $[HA(z)]_T$ involved in a complexation reaction. Hence the complexation is described by a "real constant".

$$M^{z+} + HA(z) \rightleftarrows MHA(z) \qquad \beta_z = \frac{[MHA(z)]}{[M^{z+}]_F\,[HA(z)]_F} \qquad (1),$$

where $[HA(z)]_F$ and $[M^{z+}]_F$ are respectively the concentrations of free humic sites and M^{z+} in solution. The total concentration of humic sites available to complex and neutralise a metal ion M^{z+} is written as:

$$[HA(z)]_T\ (eq/l) = \frac{(HA)\ (g/L) \times PEC\ (eq/g)}{z} \qquad (2),$$

where (HA) is the concentration of HA in g/L, PEC is the proton exchange capacity (eq/g) determined by titration.

[2] Using increasing complexation coefficient with pH.

The free humic site concentration $[HA(z)]_F$ is defined as the difference between the maximum concentration of humic sites available for the metal $LC \times [HA(z)]_T$, and the actual concentration of humic sites that are involved in the complexation [MHA(*z*)].

$$[HA(z)]_F = LC \times [HA(z)]_T - [MHA(z)] \quad (3)$$

The complexation constant is thus written as:

$$\beta_{1.z} = \frac{[MHA(z)]}{[M^{z+}]_F \left(LC \times [HA(z)]_T - [MHA(z)]\right)} \quad (4).$$

Nevertheless, in the case of moderately hydrolysed actinides (*e.g.* Am^{3+} or UO_2^{2+}), the authors have managed the metal-HA interaction increase with pH by postulating the formation of mixed complexes [52-54]:

$$M^{z+} + n\ OH^- + HA(z\text{-}n) \rightleftarrows M(OH)_nHA(z\text{-}n) \qquad \beta_{1.n.z} = \frac{[M(OH)_nHA(z\text{-}n)]}{[M^{z+}]_F\ [OH^-]^n\ [HA(z\text{-}n)]_F} \quad (5).$$

Panak *et al.* [52] have also noticed spectroscopic modifications of Cm(III) in the presence of HA with increasing pH and carbonate concentration. They postulated the occurrence of mixed carbonato species through the reaction:

$$M^{z+} + m\ CO_3^{2-} + HA(z\text{-}2m) \rightleftarrows M(CO_3)_mHA(z\text{-}2m) \beta_{1.m.z} = \frac{[M(CO_3)_mHA(z\text{-}2m)]}{[M^{z+}]_F\ [CO_3^{2-}]^m\ [HA(z\text{-}2m)]_F} \quad (6).$$

In these cases, LC is not easy to determine and the authors postulated that $LC \equiv 1$ due to the pH value close to the total ionisation of the HS ($pH \geq 6$) [52, 53].

2.2. Reinterpretation of thorium (IV) literature data through CNM

2.2.1. Formation of ThHA(IV)

The hydrolysis and carbonatation of thorium (IV) in solution is still a matter of debate [55-61]. Nevertheless, it is commonly accepted that Th^{4+} is less prone to hydrolysis than other actinides (IV). The humic complexation[3] of thorium (IV) in acidic media has been studied by Nash and Choppin [50] using liquid-liquid extraction from water.[4] From the complexation constants available in [50] taken from [55, 62], it can be calculated that the chemistry of thorium (IV) is dominated by acetate complexation.

The reaction between Th^{4+} and HA(*IV*) can be written:

[3] Humic acid from Lac Bradford

[4] Sodium acetate 0.05 M - sodium perchlorate 0.05 M in toluene with di-2-ethyhexyl phosphoric acid

$$Th^{4+} + HA(IV) \rightleftarrows ThHA(IV) \qquad \beta_{1.IV} = \frac{[ThHA(IV)]}{[Th^{4+}]_F\,[HA(IV)]_F} \qquad (7).$$

The available data can be used to calculate $\log \beta_{1.IV}$. Using the Schubert formalism [63, 64], and under the conditions that thorium is present at trace concentration, and when no HA are present, the distribution coefficient of thorium between organic and aqueous phase is written as:

$$D° = \frac{[Th]_{org}}{[Th]_{aq}} \equiv \frac{[Th]_{org}}{[Th^{4+}] \times \left(1 + \sum_{i=1}^{n} \frac{{}^*\beta_i}{[H^+]^i} + \sum_{j=1}^{m} \beta_j^{AcO} \left(\frac{[AcOH]_T}{1 + \beta^H\,[H^+]}\right)^j\right)} = \frac{[Th]_{org}}{[Th^{4+}] \times \alpha} \qquad (8).$$

were ${}^*\beta_i$ are the thorium (IV) cumulative hydrolysis constants, β_j^{AcO} are the cumulative constants for acetate complexation, β^H is the protonation constant for acetate ion and α is the complexation coefficient.

Assuming that humic complexes are not extracted in the organic phase, the distribution coefficient is thus written:

$$D \equiv \frac{[Th]_{org}}{[Th^{4+}]\left(\alpha + \beta_{1.IV}\,[HA(IV)]_F\right)} \qquad (9)$$

From equation (8) and (9), comes the expression of $\beta_{1.IV}$:

$$\beta_{1.IV} = \left(\frac{D°}{D} - 1\right)\frac{\alpha}{[HA(IV)]_F} \qquad (10).$$

Knowing that ^{230}Th is used as a tracer, the balance of humic sites is not significantly modified by the complexation and $\beta_{1.IV}$ can be expressed as:

$$\beta_{1.IV} \equiv \left(\frac{D°}{D} - 1\right)\frac{\alpha}{LC \times [HA(IV)]_T} \qquad (11).$$

The LC parameter cannot be determined straightforwardly from the available data because Th^{4+} saturation experiment was not, or rather could not, be undertaken in [50]. Hence, only the product $LC \times \beta_{1.IV}$ could be calculated.

The pH, D and $[HA]_T$ (eq/L) values from Nash and Choppin [50] are reported in Table 1. $[HA(IV)]_T$ is calculated as $[HA]_T/4$, according to the model. The values of the complexation coefficient α are obtained from the thorium acetate complexation constants β_j^{AcO} available in [50, 62], pK_a (AcO^-) = 4.5 and the thorium hydrolysis constants ${}^*\beta_i$ in [55] (Table 2).[5] A

[5] One should note that the strict application of SIT should require the knowledge of Th^{4+}/CH_3COO^- interaction parameter since the ionic medium is a mixture of CH_3COONa and $NaClO_4$.

mean value of log (LC × $\beta_{1.IV}$) = 11.7 ± 0.3 is obtained with a 95% confidence interval.[6] It is to be noted that the use of other constant sets [57, 59, 61] induces only minor changes, since the speciation of thorium (IV) is controlled by acetate complexation.

From the determination of LC in the case of neptunium (V), it has been observed that HAs from Gorleben (Gohy 573), Aldrich or Lac Bradford follow the same pattern [Fig. 8 in 65], yielding to the following expression:

$$\log LC = (0.26 \pm 0.03)\ pH - (2.72 \pm 0.02) \qquad (12).$$

Otherwise, LC seems to increase with the charge of the metal (*e.g.* Am^{3+} - pH = 4, LC = 0.216 ± 0,007 [28]; UO_2^{2+}- pH = 4, LC = 0.186 ± 0,003 [24]; NpO_2^+, pH = 7, LC = 0.13 ± 0.01 [65]). Unfortunately, the extrapolation to z = 4 seems to be unreasonable because of the residual charges greater that z carried by the metals in actinyl (V) and (VI) molecular ions [66]. Furthermore, it is known that the loading parameter of $UO_2HA(II)$ is close to the one of Am(HA(*III*) [24, 67-69]. The same behaviour was postulated in micellar exchange [70]. We propose to use LC = 0.2 in a first approximation as in the case of Am^{3+}. This leads to a value of log $\beta_{1.IV}$ = 12.4 ± 0.3 with a 95% confidence interval. Under these particular conditions, the value of LC does not seem to be as crucial as in the case of Am^{3+} [Fig. 7 in 28], as a value of LC = 0.3 would lead to a value of log $\beta_{1.IV}$ = 12.2, and log $\beta_{1.IV}$ = 12.7 when LC = 0.1. The experimental uncertainty (2.6%) is without a doubt underestimated regarding to our approximations and possible systematic errors. Consequently, a 5% uncertainty should be a better estimate, leading to log $\beta_{1.IV}$ = 12.4 ± 0.6.

The speciation of thorium (IV) using the specific interaction theory (SIT) [71], referring to the parameter in [61] (constants in Table 2) in 0.101 mol/kg water (*m*) (0.1 M $NaClO_4$), could be proposed on Figure 1 when $[HA(IV)]_T = 1.85\ 10^{-5}$ eq/L,[7] close to the value for the Gorleben site Gohy 2227 [72]. The importance of humic complexation would then be limited to pH ≤ 6.5, which is not in agreement with several environmental observations [36, 45-49].

In the framework of the CNM, the formation of a mixed hydrolysed complex could be postulated.

2.2.2. Mixed complex formation

Up to now only few studies considering mixed humic complexes of tetravalent actinides have been published. The first estimation was proposed in the case of plutonium (IV) in [73] considering the fact that more than 90% of tetravalent elements were complexed by HS in natural waters. The authors proposed the formation of $Pu(OH)_3HA(I)$ through:

$$Pu^{4+} + 3OH^- + HA(I) \rightleftarrows Pu(OH)_3HA(I) \qquad \log {}^{HA}\beta_{1.3.I} = 56{,}4 \qquad (13).$$

[6] $t_{0.95}$ = 2.201, with 12 values

[7] (HA) = 140 mg/L, PEC = 5.4 meq/g.

Up to now no validation of this estimate was done.

Recently, we studied the interaction of thorium (IV) with HS in a neutral pH range in competition with the silica surface [51]. These data could also be interpreted in the framework of the CNM. Adapting equations (8) and (9) leads to the following relations:

$$\beta_{1.3.I} = \frac{\alpha}{LC \times [HA(I)]_T \times [OH^-]^3}\left(\frac{D^\circ}{D} - 1\right) = \frac{\alpha}{LC \times [HA(I)]_T \times 10^{3\,(pH-pK_w)}}\left(\frac{D^\circ}{D} - 1\right) \qquad (14).$$

As in the case of Am^{3+}-Cm^{3+} mixed complexes, we will consider that LC ≡ 1 [52, 53]. The experimental results and estimated constants are reported in Table 3.

Contrary to log $\beta_{1.IV}$, log $\beta_{1.n.I}$ directly depends upon the hydrolysis constant set since this phenomenon controls the aqueous speciation. Mean values of log $\beta_{1.3.I}$ of 35.1 ± 0.7 [61] (Figure 2), 36.7 ± 0.8 [55] to 38.7 ± 0.8 [57] are obtained depending on the origin of the constants with 95% confidence interval. The log $\beta_{1.3.I}$ values are fairly constant in the pH range and seem to represent the pH influence on the humic complexation.

Speciation for $[HA]_T = 7.8\ 10^{-4}$ eq/L,[8] *i.e.* close to the Gorleben Gohy 2227 case, referring to [61] is proposed on Figure 3a under these assumptions. Compared with Figure 1, the predominance of humic complexes of thorium (IV) is clearly shifted by more than two pH units. When pH ≥ 9 the proportion of humic complex is still as high as 33%. If the HA concentration is reduced to $[HA]_T = 6.00\ 10^{-6}$ eq/L,[9] close to estimated value in Mont-Terri and Benken Swiss site [74] (Figure 3b), then humic complexes would represent 20% at pH = 7 and around 3% at pH = 8.

Using a 95% confidence interval, the determinations log $\beta_{1.3.I}$ at different pH values are not significantly different. Nevertheless, a slight increase could be mentioned when accounting for $Th(OH)_3HA(I)$ (Figure 2). Two hypothesis could be made in the framework of the model: the occurrence of one less hydrolysed or one more hydrolysed species: *e.g.* $Th(OH)_2HA(II)$ and $Th(OH)_4HA(0)$ respectively. The former hypothesis is impossible to assess using these experimental data since $Th(OH)_2^{2+}$ would be predominant in solution when pH ≤ 5.5 [61]. The latter hypothesis needs an adaptation of the model. Through equation (2), if $z = 0$ then $[HA(0)] \rightarrow \infty$. Hence, the boundary condition is when $z = 0$ then $[HA(0)] = [HA(I)]$.

The following equilibrium could then be proposed:

$$Th^{4+} + 4\ OH^- + HA(I) \rightleftarrows Th(OH)_4HA(I) \qquad \log \beta_{1.4.I} = \frac{[Th(OH)_4HA(I)]}{[Th^{4+}]_F\,[OH^-]^4\,[HA(I)]_F} \qquad (15)$$

The equation (14) is then rewritten as:

[8] (HA) = 140 mg/L, PEC = 5.4 meq/g, $[HA(I)] = 7.4\ 10^{-4}$ eq/L, $[HA(IV)] \approx 1.9\ 10^{-4}$ eq/L.

[9] (HA) = 0.6 mg/L, PEC = 5.4 meq/g, $[HA(I)] = 3.23\ 10^{-6}$ eq/L, $[HA(IV)] \approx 1.08\ 10^{-6}$ eq/L

$$\beta_{1.4.I} = \frac{[Th(OH)_4HA(I)]}{[Th^{4+}]_F\,[OH^-]^4\,[HA(I)]_F} \equiv \frac{\alpha}{[HA(I)]_T \times 10^{4.(pH-pK_w)}}\left(\frac{K_d^o}{K_d} - 1\right) \quad (16)$$

The calculated values of log $\beta_{1.4.I}$ are also reported in Table 3. Like in the case of log $\beta_{1.3.I}$, log $\beta_{1.4.I}$ directly depends on the hydrolysis constant set. Mean values of log $\beta_{1.4.I}$ of 41.6 ± 0.6 [61], 43.2 ± 0.6 [55] and 45.2 ± 0.6 [57] are obtained depending on the origin of the constants. Nevertheless, a slight decrease in log $\beta_{1.4.I}$ with pH could be noted (Figure 2). The data could then be described with more than one species – *e.g.* $Th(OH)_3HA(I)$ and $Th(OH)_4HA(I)$ –, but the constants could not be assessed with the experimental data.

A speciation is calculated with $[HA]_T = 7.8\ 10^{-4}$ eq/L on Figure 4a, with log $\beta_{1.4.I} = 41.6$. HA totally controls the thorium chemistry when pH ≤ 10. The proportion of humic complex is still important when (HA) is lowered to 0.3 mg/L or $[HA]_T = 1.48\ 10^{-6}$ eq/L (Swiss site, Figure 4b). This result does not seem to be in agreement with the results of the study of Glaus *et al.* [74], but one must remind that the carbonate complexation has not been taken into account.

The original sorption results in [51] could help us to opt for an hypothesis. Both D° and D values of thorium (IV) in the systems Th-SiO_2-HA are very similar at the three pH values (*i.e.* 6.75, 7.2, 7.9). This fact may indicate that the complexation properties of HA towards thorium (IV) are rather constant in the pH range. This may be in favour of the $Th(OH)_4HA(I)$ option, which implies a rather constant proportion of humic complex when pH ≥ 6.7.

2.3. Application to solubility prediction and on independent data

One could calculate the enhancement of the "theoretical" solubility of ThO_2(cr) referring to the values in [61] in the case of Gohy 2227 (Figure 5). A fairly high enhancement of thorium solubility could be prognosticated. In the case of the Swiss sites the enhancement is lower than the uncertainty of the ThO_2 solubility (data not shown). Like it has already been observed in the case or Fe, [75, 76], Al [77] and Pd [78], an increase of more than one order of magnitude could be expected. The same trend could be observed for the other actinide oxides. An experimental validation of this hypothesis is needed.

The formation of carbonate complexes of thorium is a matter of debate. Some authors proposed the limiting carbonate complex $Th(CO_3)_5^{6-}$ [56, 58, 79], as it is the case for uranium (IV) [71], plutonium (IV) [80] and neptunium (IV) [81]. From solubility experiments of ThO_2 in carbonate media, the formation of $ThCO_3(OH)_3^-$ was also proposed [58, 82] at low carbonate concentration, even if spectroscopic evidences of this species could not be obtained [82].

Even if the formation of mixed complexes is also a matter of debate [83-85], we can use these constants in order to appreciate the effects of carbonate complexation of thorium (IV) on the stability of humic complexes. We calculated a speciation for a total inorganic carbon concentration, $[TIC] = 8.2\ 10^{-3}$ *m*, $[HA]_T = 7.4\ 10^{-4}$ eq/L, using the Th^{4+} hydrolysis and carbonatation constants in [57, 58] extrapolated to 0.101 *m* (0.1 M $NaClO_4$) using the SIT parameters in [71], the associated humic constants log $\beta_{1.IV} = 12.4$, log $\beta_{1.3.I} = 38.7$ (Figure 6a)

or log $\beta_{1.4.I}$ = 45.2 (Figure 6b). When $Th(OH)_3HA(I)$ is taken into account, the mixed carbonato complex limits the domain where the humic complexation controls thorium chemistry. Nevertheless, the humic complex represents 60% of total thorium (IV) at pH = 8 (Figure 6a). Conversely, when $Th(OH)_4HA(I)$ is considered, $ThCO_3(OH)_3^-$ only decrease the proportion of $Th(OH)_4HA(I)$ to 90% (≈ 100% without carbonate, Figure 6b). This latter result seems to be more relevant of natural situations where thorium is associated to natural organic matter in the presence of carbonate ions [42, 51, 72]. The formation of mixed hydroxycarbonato complexes is not likely because of the negative charge of these complexes that are repelled by the negative charge of the humic acid entities. Particularly, this is the case for carbonato complexes of uranium (VI) [54], and for the influence of iodide onto the electrophilic substitution of iodine on phenolic moieties of HA [86, 87].

An application to the works of Glaus *et al.* [74] leads now to the same weak interaction of thorium (IV) with Mont-Terri and Benken organic matters as already calculated in [51] ($Th(OH)_4HA(I) \leq$ 3 %), Figure 6c).[10]

These reinterpretations of the literature data provide a consistent view of the environmental behaviour of thorium (IV). Nevertheless, further works are needed in order to assess these points experimentally.

In the following we will use the complexes $MHA(IV)$ with log $_{1.IV}$ = 12.4 and $M(OH)_4HA(I)$ with log $\beta_{1.4.I}$ adapted to the hydrolysis constants sets.

3. Application to redox sensitive actinide elements

The use of analogy between elements is useful when it is a matter of estimating data on difficult systems like uranium, neptunium or plutonium [1, 88, 89]. In deep geological media, these elements are supposed to be stable in their reduced form *i.e.* neptunium (IV), uranium (IV) and plutonium (IV) - plutonium (III) [81, 90]. If data on americium (III) or curium (III) and uranium (VI) exist in the literature [24, 67], there is only one communication up to now on neptunium (IV) complexation by HA in neutral pH interpreted with CNM [44]. The authors report an "increasing" constant in the case of $Np(OH)_3HA(I)$ and log $\beta_{1.4.I}$ = 52 independent of pH ($6 \leq pH \leq 9.5$). The neptunium (IV) hydrolysis data are not referred in the abstract.

If one assumes that the results obtained with thorium (IV) [51] can mimic those that may be acquired in the case of uranium (IV), neptunium (IV) or plutonium (IV), then using equation (11) and (16), with the proper α values and the hydrolysis constant extrapolated to 0.101 *m* $NaClO_4$ [71, 81], would give a reasonable estimates of $\beta_{1.IV}$ and $\beta_{1.4.I}$. we can propose the value of log $\beta_{1.4.I}$ = 49.3 in the case of neptunium (IV). This value is somewhat lower than the results of [44]. In as much, we can propose log $\beta_{1.4.z}$ values of 54.4 referring to [71] and

[10] 12.5 mg/L ≤ (NOM) ≤ 5.5 mg/L, comprising around 5% HA

52.1 referring to [81 page 323][11] in the case of uranium (IV) and plutonium (IV) respectively. One could note that these proposed constants agree with the order of affinity proposed in [91]. Furthermore, thorium (IV) and plutonium are known to have the same behaviour in presence of natural organic matter [92]. Nevertheless, readers should bear in mind that these constants are only estimates and should be used with caution.

An exercise on the chemistry of uranium, neptunium and plutonium in waters that contains high HA concentration could be proposed. The complexation constants from $Am^{3+}/Cm^{3+}/Eu^{3+}$ are very similar to one another [43, 67]. Then using $\log \beta_{1.III} = 6.2$ seems to be a fair approximation in the case of Pu^{3+} or Np^{3+}. The constants of the mixed complexes evidenced in [52, 53] can also be used without modification for Pu^{3+}, *i.e.* $\log \beta_{1.1.II} \approx 13$ and $\log \beta_{1.2.I} \approx 17.6$. In the case of the carbonato complex, the estimation of $Pu(CO_3)_m^{3-2m}$ in [93], very close to the values recommended for Am^{3+} [94], and the mixed complex postulated in [52], will be applied without any modification. The upper limit constant for the formation of mixed carbonato complex $Pu(CO_3)_2(OH)_3^{3-}$,[12] used by Vitorge and Capdevila [88] to fit the $PuO_2(s)$ solubility in carbonate media from literature was also included.

For actinyl (V) and (VI) ions, the values for neptunium (V) obtained at low concentration [25, 38, 39], and uranium (VI) [24, 54], could be directly applied to plutonium (V) and adapted to plutonium (VI). The constants calculated from the original data at 0.101 *m* $NaClO_4$ referring to plutonium (VI), neptunium (V) and uranium (VI) are also reported in Table 4. These constants were used in the analytical resolutions of the systems.

It is also reminded to the reader that the reducing capacity of HS is not taken into account in these calculations, as this behaviour is still difficult to assess [3-5] and is dependent on light exposure [9, 95].

Speciation of plutonium (Figure 7), neptunium (Figure 8) and uranium (Figure 9) was calculated for $E_H = -30$ mV/SHE, $[TIC] = 8.2\ 10^{-3}$ *m*, $6 \leq pH \leq 10$, $[HA]_T = 0$ and $5.4\ 10^{-4}$ eq/L,[13] assuming that $LC = LC(Am^{3+})$ for all humic complexes [Fig. 3 in 67] except for $MO_2HA(I)$ [Eq. 14 in 65]. As expected, under these particular conditions, mixes of redox species could be observed. For each actinide, a shift in the predominance of M(III) and M(IV) towards higher pH values in the presence of HA could be observed, due to the formation of the mixed complexes. The formation of $NpHA(III)$ or $NpOHHA(II)$ only occurs below the reduction limit of water and these complexes are not reported.

The theoretical speciation *vs.* E_H (mV/SHE) at pH = 7, $[TIC] = 8.2\ 10^{-3}$ *m* and $[HA]_T = 5.4\ 10^{-4}$ eq/L (HA) = 100 mg/L) for neptunium, plutonium and uranium (Figure 10) can also be calculated. It can be seen that neptunium could coexist as $NpO_2HA(I)$ and $Np(OH)_4HA(I)$, and that it could be totally reduced to $Np(OH)_4HA(I)$ when $E_H \leq 0$ mV/SHE (Figure 10a). This can be related with the observation from Gorleben ground waters [54]. Furthermore, the

[11] $\log {}^*\beta°(Pu(OH)_4(aq)) = -6.9$

[12] $Pu^{4+} + 2CO_3^{2-} + 3OH^- \rightleftarrows Pu(CO_3)_2(OH)_3^{2-}$, $\log \beta < 50.5$

[13] (HA) ≈ 100 mg/L

formation of NpHA(*IV*) would impede the reduction to neptunium (III) when pH ≤ 5 (data not shown).

In the case of Pu (Figure 10b), plutonium (III) humic complexation could be significant when $E_H \leq 100$ mV/SHE and may lead to mixes of plutonium oxidation states in solution, as it has already been reported [96, 97]. The other redox behaviour of plutonium reported in [10, 11] are more difficult to assess with these data. Nevertheless, different authors have measured E_H for different humic acid solutions at pH = 7: $E_H \approx +230$ mV/SHE [4]; $E_H \approx +260$ mV/SHE [98]; $300 \leq E_H$ (mV/SHE) ≤ 400 [99]; $438 \leq E_H$ (mV/SHE) ≤ 407 [100]. Under these conditions, plutonium is stable as $Pu(OH)_4HA(I)$, and plutonium (VI) or plutonium (V) introduced could be reduced and then complexed by HA.

In the case of uranium (Figure 10c), the formation of $U(OH)_4HA(I)$ could also imply a shift in the predominance of uranium (IV) towards higher pH values. The negative carbonato complexes of uranium (VI) would impede the formation of the humic complex [54, 69]. The reduction of uranium (VI) would only be possible when $E_H \leq 80$ mV/SHE. This value is higher that the measured ones [4, 98-100] and gives a plausible explanation for the absence of reaction noted by several authors [24, 25]. One should note that the behaviour of $UO_2OHHA(I)$ and $PuO_2OHHA(I)$ are not the same due to the highest value for the constant for $PuO_2CO_3(aq)$ compared to $UO_2CO_3(aq)$ [81, 94], probably due to systematic uncertainty [Vitorge, Pers. Comm.]. This cannot be considered as representative of plutonium (VI) comportment in sea water [12]. Furthermore, one can notice that there is a marked difference between the experimental data form different authors for uranium (VI) under low $CO_2(g)$ partial pressure.[14] Zeh *et al.* [54] did not evidenced relevant humic interaction when pH ≥ 9, while Glaus *et al.* [68, 69] and Laszak [101] quantified a significant interaction up to pH = 10. The humic interaction of M(VI) cations could therefore be underestimated in neutral to alkaline media. Further works are needed to ascertain this point.

Nevertheless, in the case of uranium, neither the results of Li *et al.* [102], nor those from Artinger *et al.* [26] could be assessed by this exercise. In the latter study, the authors did not observe any difference in the behaviour of uranium, introduced as uranium (VI) or uranium (IV), neither with purified HA [102], nor with Gorleben groundwater in the presence of natural organic matter at varying E_H [26].[15] Under these conditions, the uranium speciation would predict $U(OH)_4HA(I)$ as predominant species up to $E_H = -20$ mV/SHE, and carbonate uranium (VI) complexes for higher potentials (data not shown). More results on the actual interaction of uranium (IV) with natural organic matter under well-controlled redox conditions are thus required in order to assess this point.

E_H-pH diagrams could also be proposed in a closed system consisting of 10^{-10} mole actinide/kg water, 8.2 10^{-3} mole total carbonate/kg water and 100 mg HA/L (PEC = 5.4 meq/L). Here again we must recall that these diagrams are only the results of speciation

[14] $\log(pCO_2) = -6$

[15] $-200 \leq E_H$ (mV/SHE) $\leq +150$, $pCO_2 = 1\%$, pH = 7.2.

calculations and does not take into account the redox properties of HS, and cannot be considered as strict representation of actinide comportment in the presence of HS. The most striking example is the lack of plutonium (VI) humic complexation when pH ≥ 4.5 as it has been observed in sea water [12].

Finally, the ability of actinides (IV) to form colloids – so called "real-colloids" –, or to be associated with mineral and/or organic colloids – pseudo-colloids – in solution is not taken into account in this exercise [103]. The adsorption of actinides in general, and actinides (IV) in particular, on these colloidal phases is a known problem [10, 104-106]. So does is the stabilisation of mineral colloids by the sorption of organic matter [107-109]. An interesting study on this account is the one reported in Santschi *et al.* [92]. The authors clearly showed that Pu – most certainly Pu(IV) as it behave like Th(IV) – in pond release waters and stormwater runoff in Rocky Flats Environmental Technology Site is significantly associated[16] to the organic part of the colloids, < 0.5 µm in size. These organic colloids contained neither Si nor Al and only a weak amount of Fe, enhancing the fact that the natural chemistry of actinides (IV) is greatly influenced by natural organic matter. Nonetheless, the formation of humic coated surface, or so called organoclays, is still difficult to describe by available modelling approaches [110].

4. Conclusions

Through this exercise, we outlined that the use of analogy could permit to estimate the missing humic acid complexation constants for redox sensitive elements, namely uranium, neptunium and plutonium. Reinterpretations of thorium (IV) data available in the literature allowed us to have consistent data sets for this element and to represent independent environmental data. The adaptation of these data through analogy for uranium (IV), neptunium (IV) and plutonium (IV), permitted us to propose humic interaction constant that could be used for prognosticating the chemical form of redox sensitive actinides in environmental systems. The transposition of available data on uranium (VI), neptunium (V) and americium-curium-europium (III) helped us to appreciate the humic complexation of the different redox states of plutonium, neptunium and uranium. We have shown that the use of these data and analogies could permit to understand some puzzling behaviour of these elements.

Nevertheless, some results still cannot be represented as in the case of marine systems for plutonium and deep groundwater systems for uranium, enhancing the fact that more experiments are needed to ascertain the influence of natural organic matter onto the redox chemistry of this element.

[16] 7 to 66% of the total Pu pool.

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Figure Caption

Figure 1: Speciation of thorium (IV) *vs.* pH taking into account ThHA(*IV*) log $\beta_{1.IV}$ = 12.4 referring to [61]: [Th] = 10^{-10} *m*, [$NaClO_4$] = 0.101 *m*, (HA) = 140 mg/L or [HA(*IV*)] = 1.85 10^{-5} eq/L; initial experimental data from [50].

Figure 2: Determination of log $\beta_{1.3.I}$ (Eq. 14) and log $\beta_{1.4.I}$ (Eq. 16) from experimental data in [51], referring to auxiliary data in [61] (see Table 3).

Figure 3: Speciation of thorium (IV) *vs.* pH taking into account ThHA(*IV*) (log $\beta_{1.IV}$ = 12.4 from experimental data in [50]) and $Th(OH)_3HA(I)$ (log $\beta_{1.3.I}$ = 35.1 from experimental data in [51]) referring to auxiliary data in [61]: a. [$NaClO_4$] = 0.101 *m*, [HA(*I*)] = 7.8 10^{-4} eq/L, $[HA(IV)]_T$ = 1.95 10^{-4} eq/L; b. [$NaClO_4$] = 0.101 *m*, [HA(*I*)] = 1.48 10^{-6} eq/L, [HA(*IV*)] = 3.7 10^{-7} eq/L.

Figure 4: Speciation of thorium (IV) *vs.* pH taking into account $Th(OH)_4HA(I)$ with log $\beta_{1.4.I}$ = 41.6 referring to [61]: a. [$NaClO_4$] = 0.101 *m*, [HA(*I*)] = 7.8 10^{-4} eq/L, [HA(*IV*)] = 1.95 10^{-4} eq/L; b. [$NaClO_4$] = 0.101 *m*, [HA(*I*)] = 1.48 10^{-6} eq/L, [HA(*IV*)] = 0.3 10^{-6} eq/L.

Figure 5: Calculated solubility of ThO_2(cr) [$NaClO_4$] = 0.101 *m* using ThHA(*IV*) (log $\beta_{1.IV}$ = 12.4) and $Th(OH)_4HA(I)$ (log $\beta_{1.4.I}$ = 41.6), referring to auxiliary data in [61]; plain line $[HA]_T$ = 0 eq/L, dashed line $[HA]_T$ = 7.4 10^{-4} eq/L (HA = 140 mg/L).

Figure 6: Speciation of thorium (IV) *vs.* pH referring to [57, 58], log $\beta_{1.IV}$ = 12.4, [$NaClO_4$] = 0.101 *m*, [TIC] = 8.2 10^{-3} *m*, [HA(*I*)] = 7.8 10^{-4} eq/L, $[HA(IV)]_T$ = 1.9 10^{-4} eq/L; log $\beta_{1.IV}$ = 12.4; a. log $\beta_{1.3.IV}$ = 38.7; b. log $\beta_{1.4.IV}$ = 45.2; c. (HA) = 0.6 mg/L, PEC = 5.4 10^{-3}, [HA(*I*)] = 3.23 10^{-6} eq/L, [HA(*IV*)] = 1.08 10^{-6} eq/L.

Figure 7: Speciation of plutonium *vs.* pH referring to [81], log $\beta_{1.4.IV}$ = 52, E_H – 30 mV/SHE, [TIC] 8.2 10^{-3} *m*, $[HA]_T$ = 5.4 10^{-4} eq/L.

Figure 8: Speciation of neptunium *vs.* pH referring to [81], log $\beta_{1.4.IV}$ = 49.3, E_H – 30 mV/SHE, [TIC] 8.2 10^{-3} *m*, $[HA]_T$ = 5.4 10^{-4} eq/L

Figure 9: Speciation of uranium vs. pH referring to [71, 94], log $\beta_{1.4.IV}$ = 54.4, E_H – 30 mV/SHE, [TIC] 8.23 10^{-3} *m*, $[HA]_T$ = 5.4 10^{-4} eq/L.

Figure 10: Speciation of actinides 10^{-10} *m vs.* E_H (V/SHE), pH = 7, [$NaClO_4$] = 0.101 *m*, [TIC] = 8.2 10^{-3} *m* and $[HA]_T$ = 5.4 10^{-4} eq/L; a. neptunium; b. plutonium; c. uranium.

Figure 11: E_H-pH diagrams for a.) neptunium, b.) plutonium and c.) uranium species drawn with data from Table 2 for inorganic complexes and Table 4 for humic complexes. Redox properties of HS are not taken into account; [M] = 10^{-10} *m*, total carbonate = 8.2 10^{-3} *m*, (HA) = 100 mg/L, PEC = 5.4 meq/g, [$NaClO_4$] = 0.101 *m*.

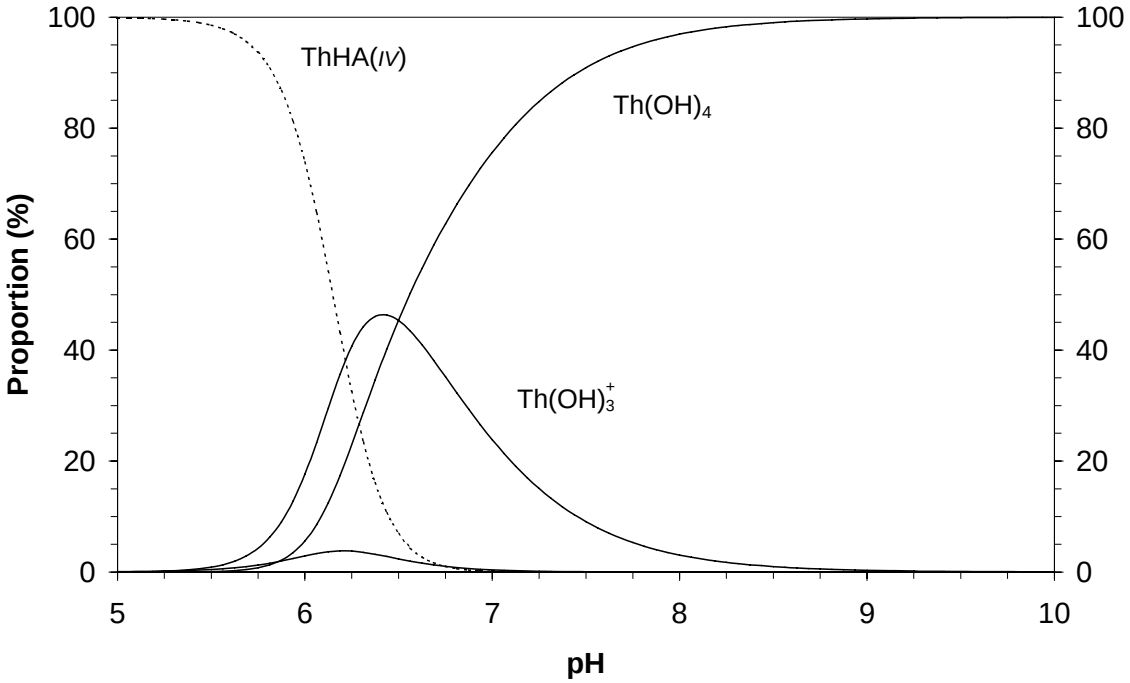
Table Caption

Table 1: Estimation of log $\beta_{1,IV}$ using CNM, from experimental data in Nash and Choppin [50].

Table 2: Complexation constant used in this study. Extrapolation at 0.101 *m* $NaClO_4$ with SIT [71], using the parameters stated in the reference.

Table 3: Estimation of the stability constants for $Th(OH)_3HA(l)$ and $Th(OH)_4HA(l)$ from experimental data in [51] referring to [61]. Uncertainties are 95% confidence interval.[a]

Table 4: Stability constants for humic complexes used in this study. The constants that take into account the reduction of M(VI) are calculated using the data from Table 2.



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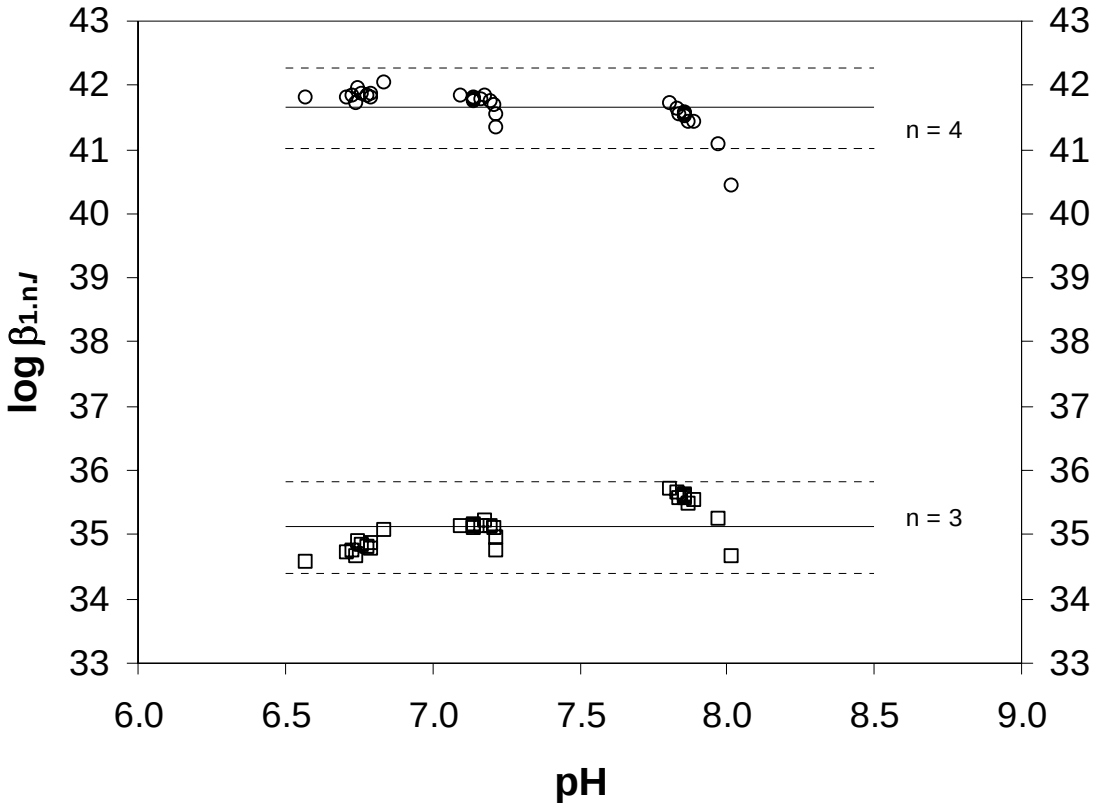

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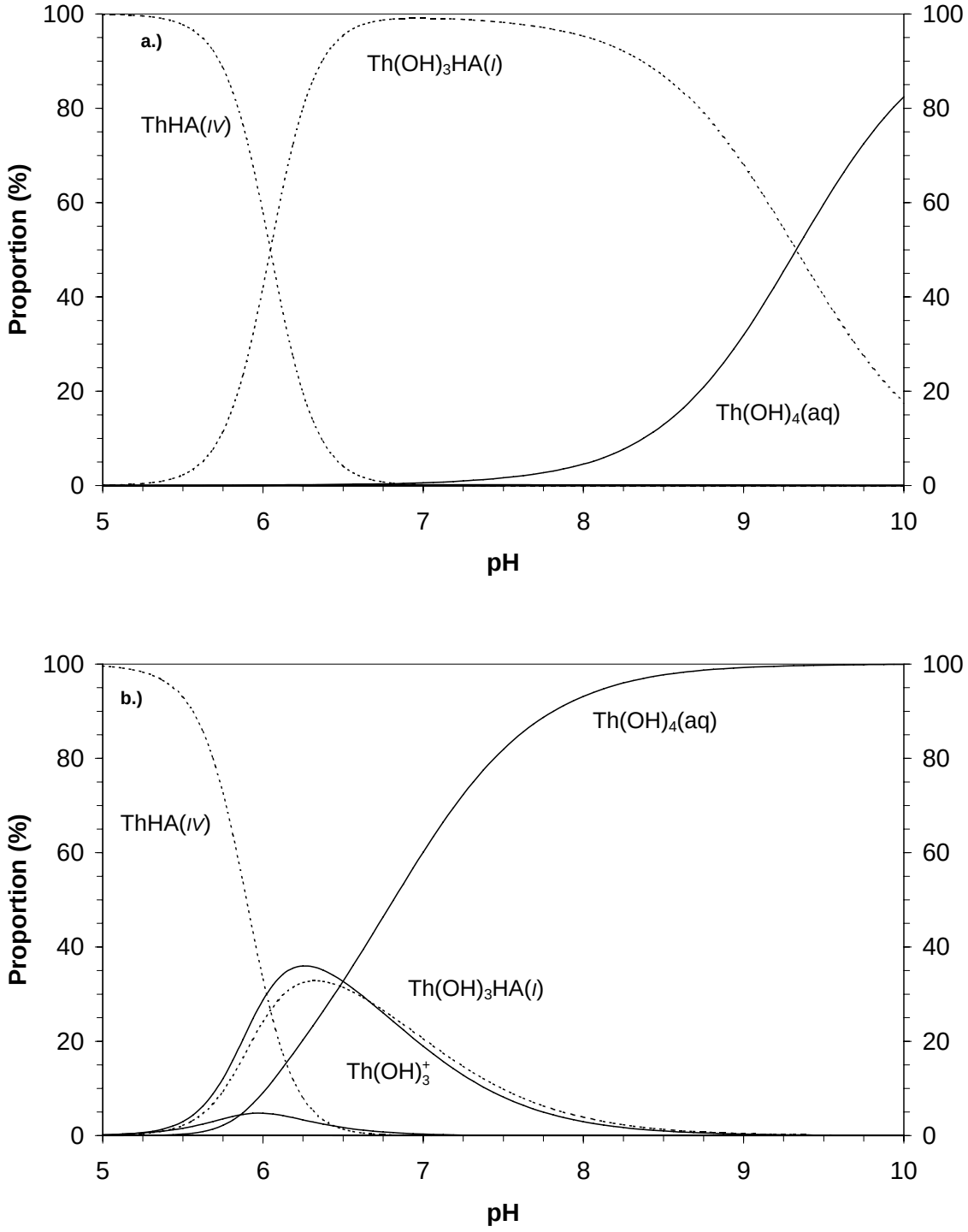

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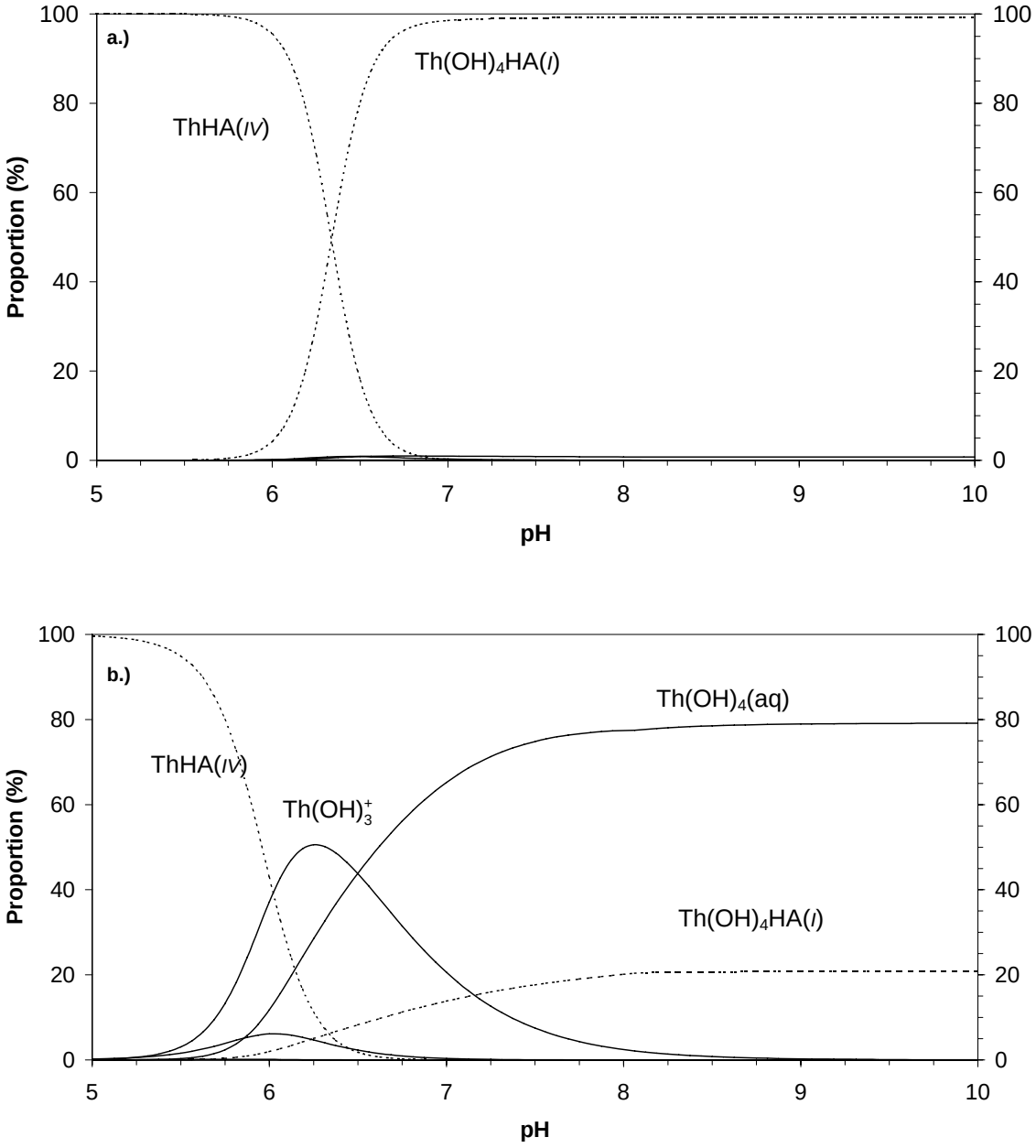

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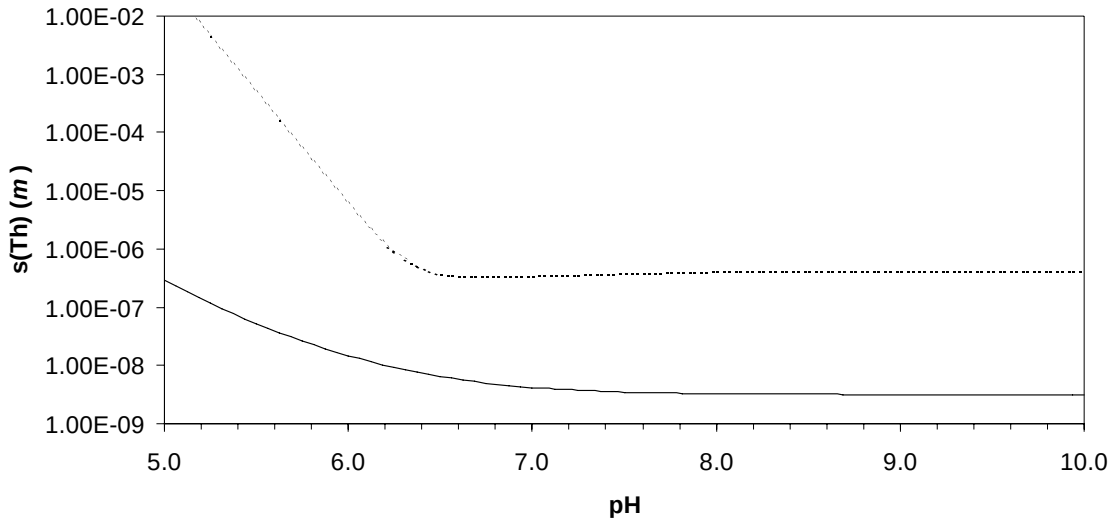

Figure 5: Calculated solubility of ThO_2(cr) [$NaClO_4$] = 0.101 *m* using ThHA(*IV*) (log $\beta_{1.IV}$ = 12.4) and $Th(OH)_4HA$(*I*) (log $\beta_{1.4.I}$ = 41.6), referring to auxiliary data in [61]; plain line $[HA]_T$ = 0 eq/L, dashed line $[HA]_T$ = 7.4 10^{-4} eq/L (HA = 140 mg/L).

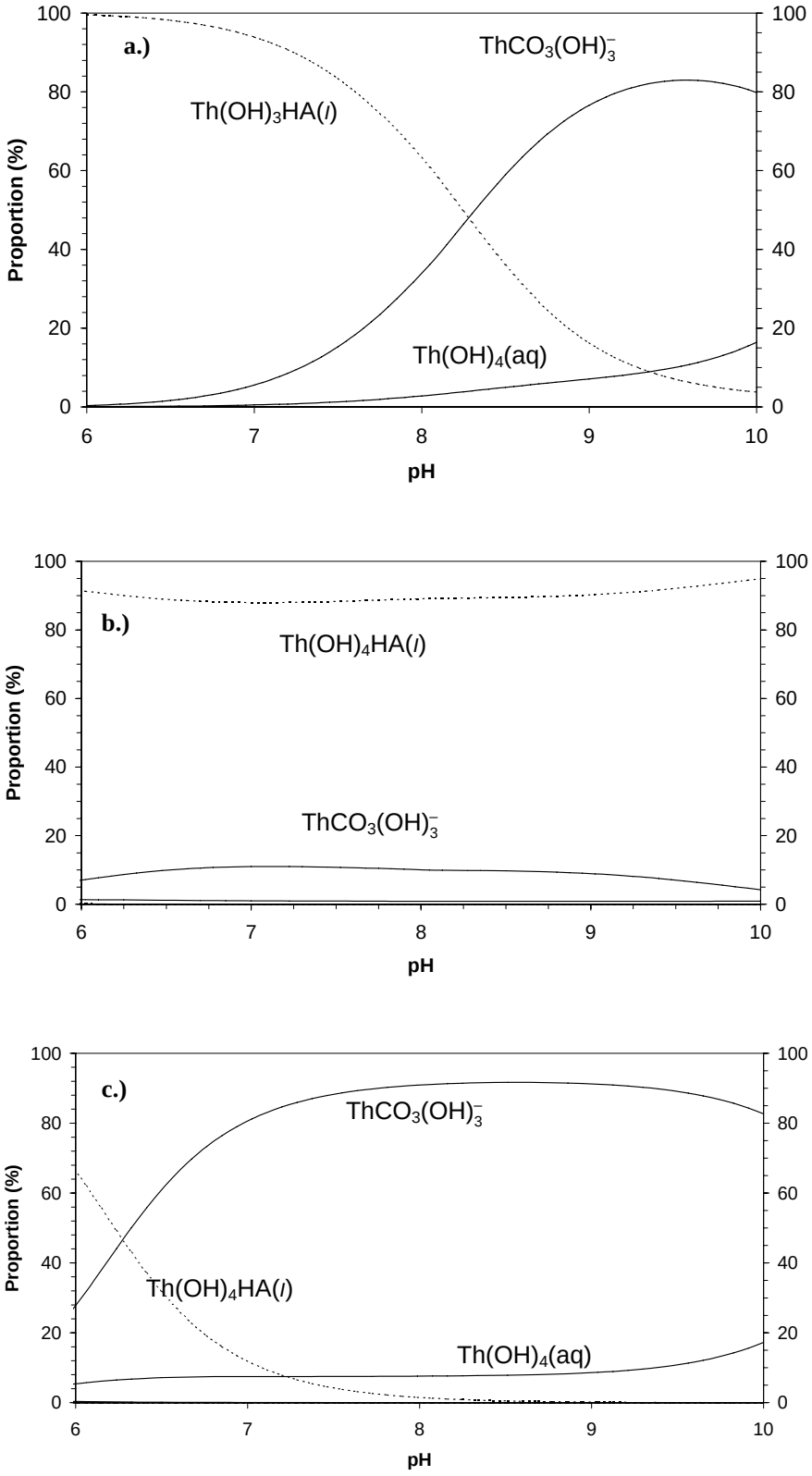

Figure 6: Speciation of thorium (IV) *vs.* pH referring to [57, 58], log $\beta_{1.IV}$ = 12.4, [$NaClO_4$] = 0.101 *m*, [TIC] = 8.2 10^{-3} *m*, [HA(*l*)] = 7.8 10^{-4} eq/L, [HA(*IV*)]$_T$ = 1.9 10^{-4} eq/L; log $\beta_{1.IV}$ = 12.4; a. log $\beta_{1.3.IV}$ = 38.7; b. log $\beta_{1.4.IV}$ = 45.2; c. (HA) = 0.6 mg/L, PEC = 5.4 10^{-3}, [HA(*l*)] = 3.23 10^{-6} eq/L, [HA(*IV*)] = 1.08 10^{-6} eq/L.

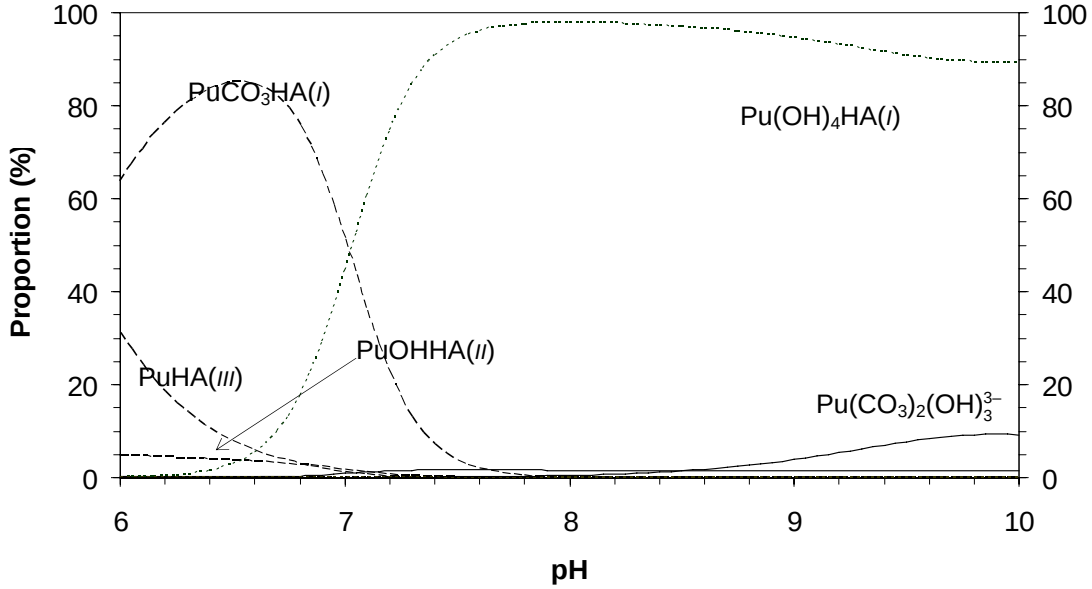

Figure 7: Speciation of plutonium *vs.* pH referring to [81], log $\beta_{1.4.IV}$ = 52, E_H = – 30 mV/SHE, [TIC] = 8.2 10^{-3} *m*, $[HA]_T$ = 5.4 10^{-4} eq/L.

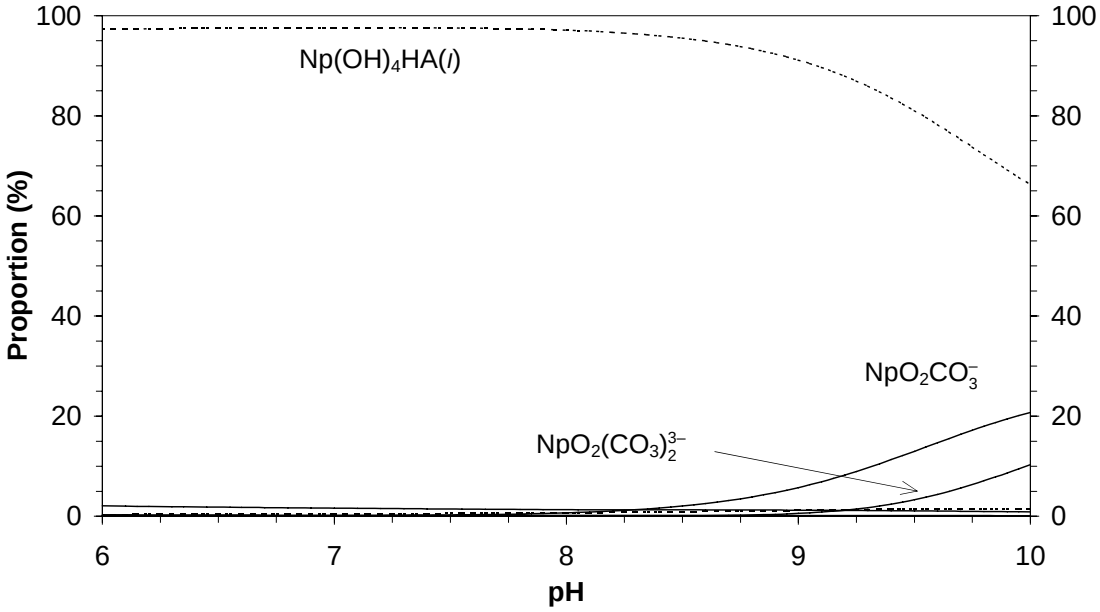

Figure 8: Speciation of neptunium *vs.* pH referring to [81], log $\beta_{1.4.IV}$ = 49.3, E_H = – 30 mV/SHE, [TIC] = 8.2 10^{-3} *m*, $[HA]_T$ = 5.4 10^{-4} eq/L

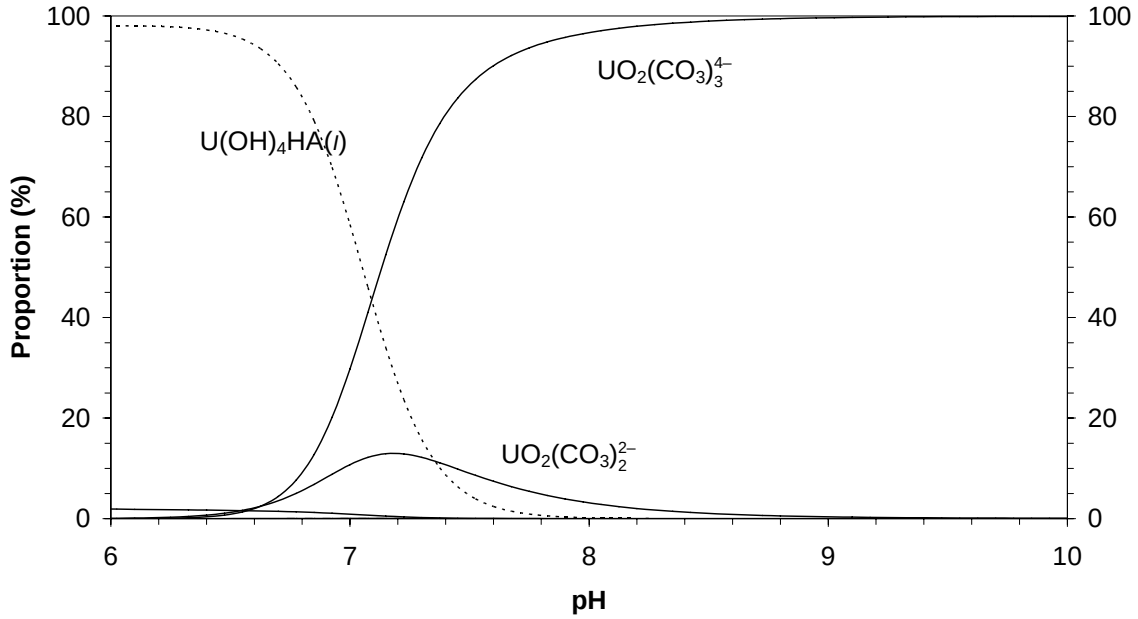

Figure 9: Speciation of uranium vs. pH referring to [71, 94], log $\beta_{1.4.IV}$ = 54.4, E_H = – 30 mV/SHE, [TIC] = 8.23 10^{-3} *m*, $[HA]_T$ = 5.4 10^{-4} eq/L.

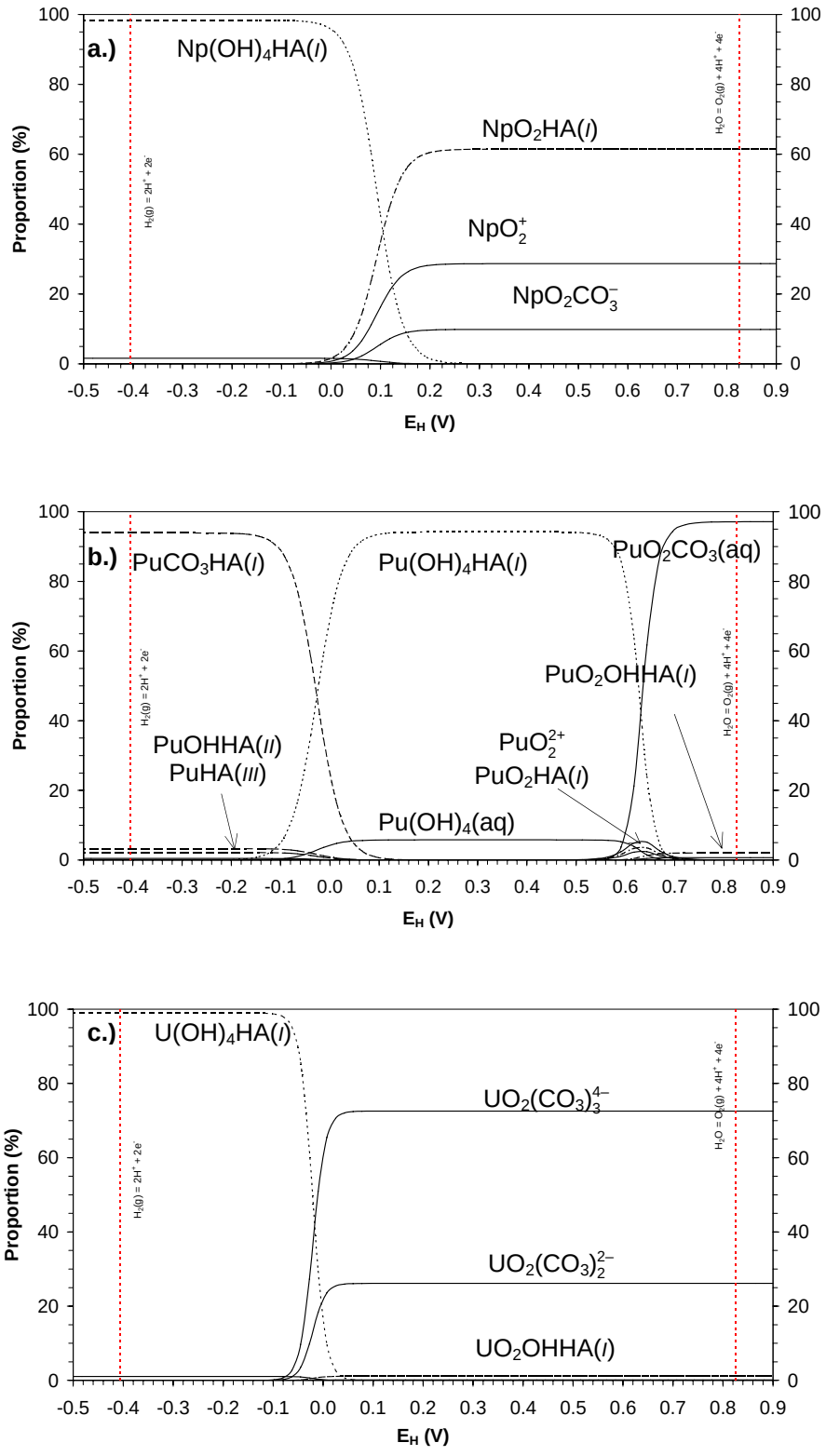

Figure 10: Speciation of actinides 10^{-10} *m vs.* E_H (V/SHE), pH = 7, [$NaClO_4$] = 0.101 *m*, [TIC] = $8.2\ 10^{-3}$ *m* and $[HA]_T = 5.4\ 10^{-4}$ eq/L; a. neptunium; b. plutonium; c. uranium.

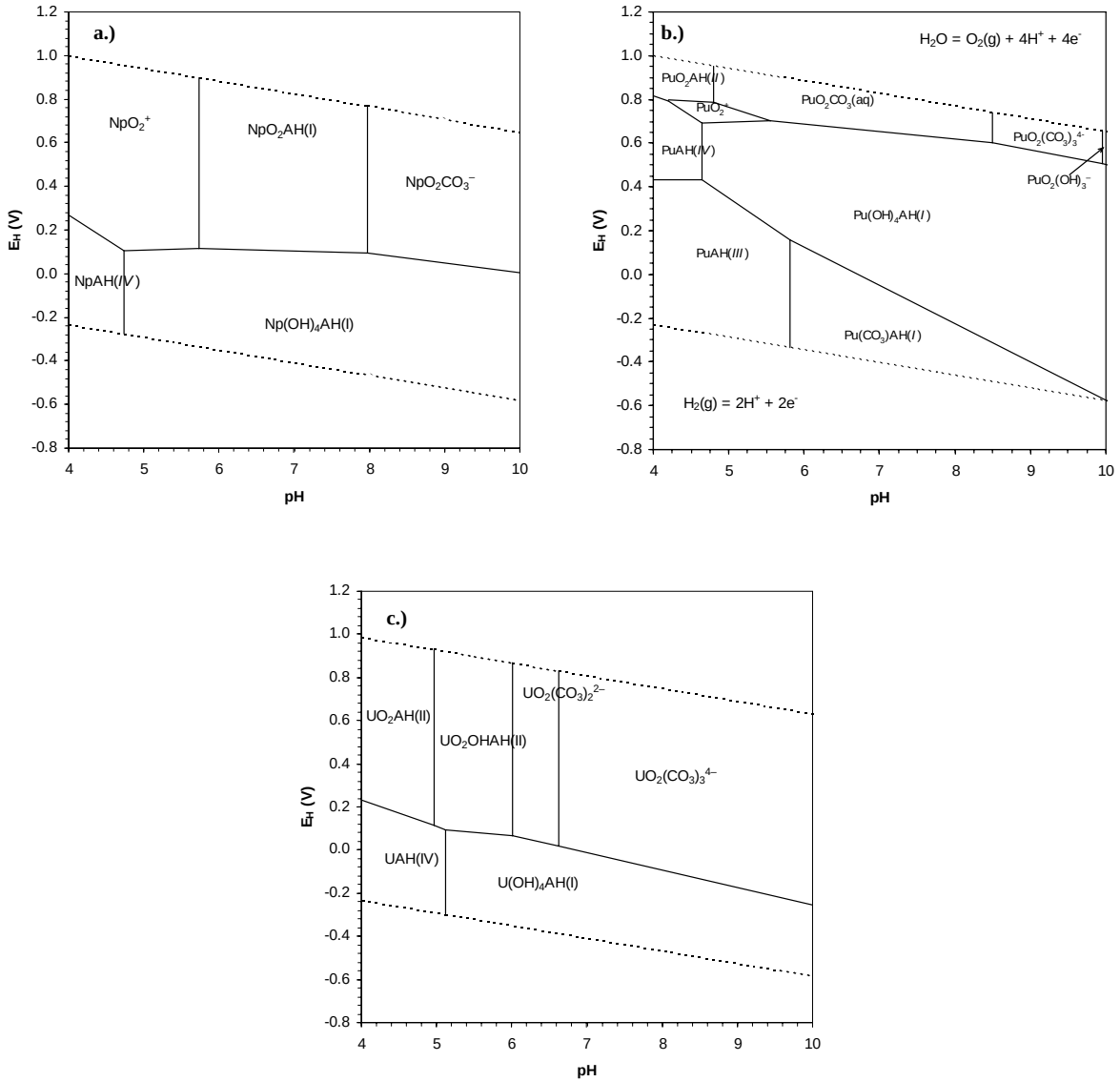

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Table 1: Estimation of log $\beta_{1.IV}$ using CNM, from experimental data in Nash and Choppin [50].

pH	D	$[HA]_T$	$[HA(IV)]$	$[AcO^-]$	α	$\frac{D^\circ}{D} - 1$	$\beta_{1.IV} \times LC$	$\log (\beta_{1.IV} \times LC)$
3.98	31.48			$1.16\ 10^{-2}$	$9.46\ 10^{3}$			
3.98	33.75							
3.937	2.170	$1.48\ 10^{-6}$	$3.58\ 10^{-7}$	$1.07\ 10^{-2}$	$7.60\ 10^{3}$	13.51	$2.87\ 10^{11}$	11.46
3.937	2.195					14.38	$3.05\ 10^{11}$	11.48
3.939	1.446	$1.98\ 10^{-6}$	$4.77\ 10^{-7}$	$1.08\ 10^{-2}$	$7.68\ 10^{3}$	20.77	$3.34\ 10^{11}$	11.52
3.939	1.423					22.71	$3.65\ 10^{11}$	11.56
3.93	1.120	$2.47\ 10^{-6}$	$5.97\ 10^{-7}$	$1.06\ 10^{-2}$	$7.34\ 10^{3}$	27.11	$3.33\ 10^{11}$	11.52
3.93	1.086					30.08	$3.70\ 10^{11}$	11.57
3.961	0.362	$4.95\ 10^{-6}$	$1.20\ 10^{-6}$	$1.12\ 10^{-2}$	$8.59\ 10^{3}$	85.91	$6.17\ 10^{11}$	11.79
3.961	0.380					87.90	$6.31\ 10^{11}$	11.80
3.928	0.219	$7.38\ 10^{-6}$	$1.78\ 10^{-6}$	$1.06\ 10^{-2}$	$7.26\ 10^{3}$	142.42	$5.80\ 10^{11}$	11.76
3.928	0.218					154.06	$6.28\ 10^{11}$	11.80
3.922	0.147	$9.88\ 10^{-6}$	$2.39\ 10^{-6}$	$1.05\ 10^{-2}$	$7.04\ 10^{3}$	212.61	$6.27\ 10^{11}$	11.80
3.922	0.155					217.07	$6.40\ 10^{11}$	11.81
								$\log(\overline{\beta_{1.IV} \times LC}) \pm s_{95\%} = 11.7 \pm 0.3$

Table 2: Complexation constant used in this study. Extrapolation at 0.101 *m* $NaClO_4$ with SIT [71], using the parameters stated in the reference.

Equilibrium	log K [71]	Th		U [71, 94]	Np [81]	Pu [81]
$CO_2(aq) + H_2O \rightleftarrows HCO_3^- + H^+$	–6.15					
$HCO_3^- \rightleftarrows CO_3^{2-} + H^+$	–9.90					
$H_2O \rightleftarrows H^+ + OH^-$	–13.80					
$M^{3+} + H_2O \rightleftarrows MOH^{2+} + H^+$					–7.24	–7.34
$M^{3+} + 2H_2O \rightleftarrows M(OH)_2^+ + 2H^+$						–15.66
$M^{3+} + CO_3^{2-} \rightleftarrows MCO_3^+$						6.21 [81, 93]
$M^{3+} + 2CO_3^{2-} \rightleftarrows M(CO_3)_2^-$						10.69 [81, 93]
		[62]				
$M^{4+} + AcO^- \rightleftarrows MOAc^{3+}$		4.04				
$M^{4+} + 2AcO^- \rightleftarrows M(OAc)_2^{2+}$		7.33				
$M^{4+} + 3AcO^- \rightleftarrows M(OAc)_3^+$		9.47				
$M^{4+} + 4AcO^- \rightleftarrows M(OAc)_4$		11.00				
		[61]	[57, 58]			
$M^{4+} + H_2O \rightleftarrows MOH^{3+} + H^+$		–2.85	–3.79	–1.18	–0.93	–1.45
$M^{4+} + 2H_2O \rightleftarrows M(OH)_2^{2+} + 2H^+$		–7.08				
$M^{4+} + 3H_2O \rightleftarrows M(OH)_3^+ + 3H^+$		–12.30	–10.38			
$M^{4+} + 4H_2O \rightleftarrows M(OH)_4 + 4H^+$		–18.80	–15.16	–6.00	–11.09	–8.27
$M^{4+} + 5CO_3^{2-} \rightleftarrows M(CO_3)_5^{6-}$			32.27	33.94	35.58	34.07
$M^{4+} + CO_3^{2-} + 3H_2O \rightleftarrows MCO_3(OH)_3^- + 3H^+$			–2.18			
$M^{4+} + 2CO_3^{2-} + 3H_2O \rightleftarrows M(CO_3)_2(OH)_3^{3-} + 3H^+$						7.22 [88]
$MO_2^+ + H_2O \rightleftarrows MO_2OH + H^+$					–11.29	–9.72
$MO_2^+ + CO_3^{2-} \rightleftarrows MO_2CO_3^-$					4.58	4.72
$MO_2^+ + 2CO_3^{2-} \rightleftarrows MO_2(CO_3)_2^{3-}$					6.61	6.39
$MO_2^{2+} + H_2O \rightleftarrows MO_2OH^+ + H^+$				–5.38		–5.71
$MO_2^{2+} + 2H_2O \rightleftarrows MO_2(OH)_2 + 2H^+$				–10.53		–13.40
$MO_2^{2+} + 3H_2O \rightleftarrows MO_2(OH)_3^- + 3H^+$				–19.19		–19.19 [88]
$MO_2^{2+} + CO_3^{2-} \rightleftarrows MO_2CO_3$				8.80		10.76
$MO_2^{2+} + 2CO_3^{2-} \rightleftarrows MO_2(CO_3)_2^{2-}$				16.16		13.66
$MO_2^{2+} + 3CO_3^{2-} \rightleftarrows MO_2(CO_3)_3^{4-}$				21.66		17.76
$MO_2^+ + ½\ H_2 + 4H^+ \rightleftarrows M^{4+} + 2H_2O + H^+$					11.41	
$MO_2^+ + H_2(g) + 4H^+ \rightleftarrows M^{3+} + 2H_2O + 2H^+$					14.14	
$MO_2^{2+} + ½\ H_2 \rightleftarrows MO_2^+ + H^+$						15.52
$MO_2^{2+} + H_2 + 4H^+ \rightleftarrows M^{4+} + 2H_2O + 2H^+$				9.94		34.13
$MO_2^{2+} + 3/2\ H_2 + 4H^+ \rightleftarrows M^{3+} + 2H_2O + 3H^+$						51.12

Following the recommendation in [71], H^+ issued from the hydrogen oxidation are not taken into account in Δz^2 and $\Delta\varepsilon$, and are thus written in italic.

Table 3: Estimation of the stability constants for $Th(OH)_3HA(i)$ and $Th(OH)_4HA(i)$ from experimental data in [51] referring to [61]. Uncertainties are 95% confidence interval.[a]

pH	[HA(*i*)]	R(%)	K_d	α	log $\beta_{1.3.i}$	log $\beta_{1.4.i}$
7.91	0	0.857	$2.395\ 10^4$			
8.02	$1.14\ 10^{-5}$	0.842	$2.133\ 10^4$	$1.97\ 10^{13}$	34.7	40.4
7.97	$2.27\ 10^{-5}$	0.744	$1.165\ 10^4$	$1.25\ 10^{13}$	35.3	41.1
7.87	$3.41\ 10^{-5}$	0.578	$5.469\ 10^3$	$5.00\ 10^{12}$	35.5	41.4
7.89	$4.55\ 10^{-5}$	0.511	$4.184\ 10^3$	$6.00\ 10^{12}$	35.5	41.4
7.86	$5.68\ 10^{-5}$	0.430	$3.012\ 10^3$	$4.57\ 10^{12}$	35.6	41.5
7.86	$6.54\ 10^{-5}$	0.368	$2.331\ 10^3$	$4.57\ 10^{12}$	35.6	41.6
7.86	$7.67\ 10^{-5}$	0.347	$2.122\ 10^3$	$4.57\ 10^{12}$	35.6	41.5
7.84	$8.53\ 10^{-5}$	0.332	$1.986\ 10^3$	$3.81\ 10^{12}$	35.6	41.5
7.81	$1.14\ 10^{-4}$	0.207	$1.042\ 10^3$	$2.90\ 10^{12}$	35.7	41.7
7.83	$1.71\ 10^{-4}$	0.176	$8.549\ 10^2$	$3.47\ 10^{12}$	35.7	41.6
					35.5 ± 0.7	41.4 ± 0.8
7.31	0	0.756	$1.243\ 10^4$			
7.22	$1.14\ 10^{-5}$	0.630	$6.825\ 10^3$	$1.44\ 10^{10}$	34.8	41.3
7.20	$2.27\ 10^{-5}$	0.377	$2.420\ 10^3$	$1.20\ 10^{10}$	35.1	41.7
7.14	$3.41\ 10^{-5}$	0.298	$1.698\ 10^3$	$7.10\ 10^9$	35.1	41.8
7.17	$4.55\ 10^{-5}$	0.242	$1.279\ 10^3$	$9.24\ 10^9$	35.1	41.8
7.18	$5.68\ 10^{-5}$	0.187	$9.221\ 10^2$	$1.01\ 10^{10}$	35.2	41.8
7.14	$6.54\ 10^{-5}$	0.182	$8.920\ 10^2$	$7.10\ 10^9$	35.1	41.8
7.10	$7.67\ 10^{-5}$	0.149	$7.012\ 10^2$	$5.00\ 10^9$	35.1	41.8
7.14	$8.53\ 10^{-5}$	0.140	$6.513\ 10^2$	$7.10\ 10^9$	35.2	41.8
7.21	$1.14\ 10^{-4}$	0.137	$6.348\ 10^2$	$1.31\ 10^{10}$	35.1	41.7
7.22	$1.71\ 10^{-4}$	0.129	$5.917\ 10^2$	$1.44\ 10^{10}$	35.0	41.5
					35.1 ± 0.3	47.7 ± 0.4
6.72	0	0.937	$5.909\ 10^4$			
6.76	$1.13\ 10^{-5}$	0.855	$2.355\ 10^4$	$2.31\ 10^8$	34.7	41.7
6.73	$2.27\ 10^{-5}$	0.662	$7.844\ 10^3$	$5.34\ 10^8$	35.1	42.0
6.74	$3.41\ 10^{-5}$	0.690	$8.888\ 10^3$	$2.12\ 10^8$	34.8	41.8
6.78	$4.55\ 10^{-5}$	0.673	$8.236\ 10^3$	$5.71\ 10^7$	34.6	41.8
6.76	$5.68\ 10^{-5}$	0.555	$4.982\ 10^3$	$3.50\ 10^8$	34.9	41.9
6.74	$6.53\ 10^{-5}$	0.560	$5.085\ 10^3$	$3.50\ 10^8$	34.8	41.8
6.76	$7.67\ 10^{-5}$	0.504	$4.067\ 10^3$	$3.22\ 10^8$	34.8	41.8
6.72	$8.53\ 10^{-5}$	0.502	$4.039\ 10^3$	$1.80\ 10^8$	34.7	41.8
6.76	$1.14\ 10^{-4}$	0.364	$2.289\ 10^3$	$2.51\ 10^8$	34.9	41.9
6.74	$1.71\ 10^{-4}$	0.311	$1.804\ 10^3$	$2.72\ 10^8$	34.8	41.9
					34.8 ± 0.3	41.9 ± 0.2
					35.1 ± 0.7	41.6 ± 0.6

[a] $\log\ \overline{\beta}\ \pm t_{0.95}.\sigma$, with $t_{0.95} = 2.262$ for 10 values (9 degrees of freedom), and $t_{0.95} = 2.045$ for 30 values (29 degrees of freedom).

Table 4: Stability constants for humic complexes used in this study. The constants that take into account the reduction of M(VI) are calculated using the data from Table 2.

Equilibrium	log $\beta_{n.m.z}$		
	Pu	**Np**	**U**
M^{3+} + HA(*III*) ⇄ MHA(*III*)	6.2		
MO_2^{2+} + *3/2* H_2 + $4H^+$ + HA(*III*) ⇄ MHA(*III*) + 2 H_2O + *3* H^+	57.3	20.3	
M^{3+} + OH^- + HA(*II*) ⇄ MOHHA(*II*)	13		
MO_2^{2+} + *3/2* H_2 + $3H^+$ + HA(*II*) ⇄ MOHHA(*II*) + H_2O + *3* H^+	50.3	13.3	
M^{3+} + 2 OH^- + HA(*I*) ⇄ $M(OH)_2HA$(*I*)	17.6		
MO_2^{2+} + *3/2* H_2 + $2H^+$ + HA(*II*) ⇄ $M(OH)_2HA$(*II*) + *3* H^+	41.1		
M^{3+} + CO_3^{2-} + HA(*I*) ⇄ MCO_3HA(*I*)	12.4		
MO_2^{2+} + *3/2* H_2 + $4H^+$ + CO_3^{2-} + HA(*I*) ⇄ MCO_3HA(*I*) + 2 H_2O + *3* H^+	63.5		
M^{4+} + HA(*IV*) ⇄ MHA(*IV*)	16.0	13.2	18.2
MO_2^{2+} + H_2 + $4H^+$ + HA(*IV*) ⇄ MHA(*IV*) + 2 H_2O + 2 H^+	50.1	24.6	28.1
M^{4+} + 4 OH^- + HA(*I*) ⇄ $M(OH)_4HA$(*I*)	52.0	49.3	54.4
MO_2^{2+} + H_2 + 2 H_2O + HA(*I*) ⇄ $M(OH)_4HA$(*I*) + *2* H^+	30.9	5.5	9.0
MO_2^+ + HA(*I*) ⇄ MO_2HA(*I*)	4.6	4.6	
MO_2^{2+} + ½ H_2 + HA(*I*) ⇄ MO_2HA(*I*) + H^+	20.0		
MO_2^{2+} + HA(*II*) ⇄ MO_2HA(*II*)	6.2		6.2
MO_2^{2+} + OH^- + HA(*I*) ⇄ MO_2OHHA(*I*)	14.05		14.7

Following the recommendation in [71], H^+ issued from the hydrogen oxidation are not taken into account in Δz^2 and $\Delta\varepsilon$, and are thus written in italic.